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(54) Title: BIAXIALLY ORIENTED PENBB FILM COATED WITH ANTISTATIC COATINGS (57) Abstract <p>The invention concerns an antistatic, mono- or multilayer bi-axially oriented copolyester film, wherein the copolyester is PENBB and wherein at least one surface of the film has been coated with an antistatic coating composition containing (I) a quarternary ammonium salt (QAS) and/or (II) a two component system consisting of: (a) an acrylate, styrene-derivative or acrylonitrile, and (b) an ethylenically unsaturated sulfonate salt and/or (III) an organically substituted phosphate. PENBB is a copolyester containing units of formula (1).</p> <div style="text-align: center;">  (1) </div>		

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BIAXIALLY ORIENTED PENBB FILM COATED WITH ANTISTATIC COATINGS**Background of the Invention**

5 This invention is directed to an improved polyester film having excellent antistatic properties as well as improved mechanical strength and stiffness, and dimensional stability and to a method for producing such film. More specifically, the invention deals with improved biaxially oriented copolyester films having improved antistatic properties coupled with altered surface properties which render the film printable or coatable with additional
10 coatings such as photosensitive compositions, while exhibiting the improved dimensional and mechanical properties.

The growth of the packaging, reprographic, microfilm and magnetic tape markets has significantly increased the utilization of polyester film materials in these fields, particularly biaxially oriented polyethylene terephthalate (PET). However, there are still some problems with PET films. Some
15 of the problems encountered in these applications are caused by the limits of the PET material. Specifically, there is a need for greater stiffness (tensile modulus) and tensile strength, improved dimensional stability, UV resistance and hydrolytic stability. Another problem associated with the use of such film
20 is the tendency of these materials to accumulate an electrostatic charge on the surface as the result of handling or processing of the film, particularly at low relative humidity. This electrostatic charge attracts not only dust and other contaminants, but additionally attracts other film. For instance, in the case of PET film supports, electrostatic charges may interfere with the collating, sorting and developing of microfiche cards or transparent supports and
25 cause these materials to stick together.

To overcome this serious problem, antistatic films have been developed. Antistatic films are usually formed by the application of an antistatic coating onto the surface of the film. Many of these coatings have successfully
30 reduced the electrostatic charging properties of the film to satisfactorily low levels. However, many of these coatings can cause blocking. That is, the film coated with an antistatic layer has a coefficient of friction high

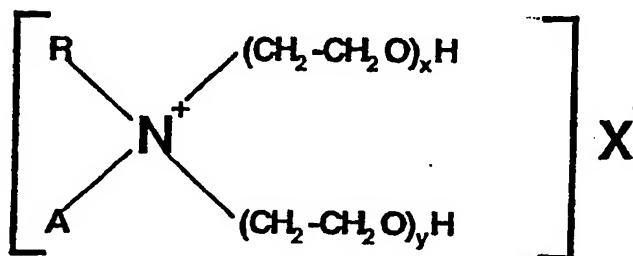
enough so that one layer of the film does not slip over another or over rollers and other equipment over which the film moves during manufacture and use.

Another problem arising from the coating of an antistatic layer onto a surface of a film is the decreased clarity resulting therefrom. This property, usually termed as haze, is very important in microfilm applications. Microfilm must be readable. Light is projected through the film so that the viewer may read the information printed on the film. Poor clarity results in fuzziness and difficulty in reading because of loss of light intensity.

Yet a third problem associated with the application of an antistatic coating is its ability to remain adhered to the surface of the film, particularly where the film is later treated with printing or coating compositions.

Various antistatic coatings are disclosed in the prior art. For example, U.S. Pat. No. 4,214,035 teaches the application to PET film of an antistatic coating based on a mixture of stearamidopropyldimethyl- β -hydroxyethylammonium nitrate and a cross-linkable acrylic terpolymer binder, present in an approximately three to one ratio respectively. The antistatic surface of such film is not readily susceptible to the application of additional coatings, particularly in reprographic applications.

British Pat. No. 1,558,064 discloses the use of certain quarternary ammonium salts as an antistatic coating for polyolefin film such as polypropylene. These salts have the formula:



wherein A is lower alkyl, R is an aliphatic radical having 1 to 22 carbons, x and y are integers having the sum of 2 to 5, and X⁻ is an anion. The utilization of this material as disclosed in the patent, aside from its effectiveness as

an antistatic, does not resolve the problem of the lack of adhesion of additional coatings over the antistatic coating.

Accordingly, it is an object of this invention to provide plastic film material having improved antistatic properties as well as good blocking properties and low haze.

Another object is to provide an antistatic coating on at least one surface of a film providing improved dimensional and mechanical stability, which coating may provide a suitable base coat or primer coat for the application of additional coatings.

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Summary of the Invention

The present invention relates to an antistatic biaxially oriented PENBB film and the process for producing the film. More particularly, the present invention relates to an antistatic biaxially oriented PENBB film having excellent antistatic properties, and/or excellent adhesivity, and excellent mechanical and dimensional stability, and a process for producing the film.

15

The improved mechanically and dimensionally stable PENBB base film of the present invention carries an antistatic coating composition containing

- I) a quarternary ammonium salt and/or
- II) a two-component composition consisting of
 - a) an acrylate, styrene derivative or acrylonitril and
 - b) an ethelenically unsaturated sulfonate salt and/or
- III) an organically substituted phosphate.

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Similar coatings are disclosed in U.S. Patent 4,642,263 and European Applications 0 435 080 and 0 442 607. U.S. Patent No. 3,008,934 discloses copolyesters containing as acid derived units 4,4'-bibenzoate and a host of other dicarboxylates including 2,6-naphthalic dicarboxylate. It also discloses oriented fibers and films prepared from these copolyesters, however, biaxially oriented PENBB films are not disclosed or envisioned. In particular, those films with improved stiffness (tensile modulus) and tensile strength in both MD and TD as well as thermostability, UV stability, hydrophobicity,

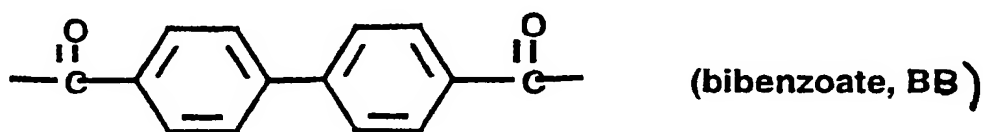
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dimensional stability and impermeability toward gases in comparison to PET film are not disclosed in U.S. Patent No. 3,008,934.

Detailed Description of the Invention and Its preferred Embodiments

5 The biaxially oriented copolyester film base for the purpose of this invention is made from PENBB.

PENBB as mentioned hereinbefore is a copolyester containing as acid-derived unit at least 5 mole percent of a radical of the formula:



10 In the case that more than 10 mole percent of terephthalic acid derived radicals are present in the copolymer, the content of bibenzoate derived units is at least 25 mole percent. Films of these copolyesters are mentioned in the unpublished German Patent Application P 4224161.8, which is incorporated herein by reference. Preferably PENBB is a copolyester wherein at least 80
15 mole percent of the acid derived units (NBB) consist of bibenzoate (20 to 80 mole percent, preferably 40 to 60 mole percent) and naphthalate (80 to 20 mole percent, preferably 60 to 40 mole percent). The remaining 20 or less mole percent may consist of other acid derived units, which e.g. affect the melting point or the crystallization kinetics. Preferably at least 80 mole
20 percent of the diol-derived units consist of -O(CH₂)₂-O-units. The remaining 20 or less mole percent consist of other diol-derived units, which e.g. may also affect the melting point or the crystallization kinetics. It may also be desirable to replace minor amounts of the acid- and/or diol-derived units with hydroxycarboxylic-acid-derived units, e.g. such derived from p-hydroxybenzoic acid. In order to achieve the desired mechanical properties in the biaxially oriented PENBB film it is recommended that the IV value (inherent viscosity, as measured in a 1 : 1 weight-ratio mixture of pentafluorophenol and hexafluoroisopropanol at a concentration of 0.2 g/dl and a temperature of 25
25

°C) of the PENBB polymer after extrusion be > 0.5 dl/g and preferably > 0.55 dl/g.

To produce the film, the polymer melt is extruded through a die onto a chill roll where it solidifies, is then biaxially oriented, heat set, optionally post treated and the wound on a roll. For a multilayer film known methods for coextrusion, in-line or off-line coating can be used. The solidified film as extruded on the chill roll should be obtained in an essentially amorphous state. To achieve this, the melt film must be pinned to the chill roll by a known method such as electrostatic pinning or vacuum, air knife or the like.

The biaxial orientation of the film is achieved by stretching the film at elevated temperature in the machine (MD) and transverse direction (TD). This stretching can be either simultaneous or sequential. In the case of sequential stretching the first stretching step can be in either MD or TD, followed by stretching in the other direction. The orientation in MD can also be achieved in several steps, either one after another prior to stretching in TD, or before and after the TD stretching. Preferred temperatures for stretching lie between the glass transition temperature (T_g) and about 30°C above the cold crystallization temperature (T_{cc}) of the PENBB copolymer composition in use (both temperatures can easily be measured on amorphous films by DSC). The total stretch ratios (λ) in MD and TD lie between 1 : 2 and 1 : 10, preferably between 1 : 2.5 and 1 : 5. The product of the total stretch ratios should be between 1 to 30 preferably between 5 to 20. Biaxial drawing is performed such that the birefringence is < 0.2 , preferably < 0.1 to ensure adequately isotropic properties. Birefringence as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

In order to optimize shrinkage properties, relaxation steps can be included in the orientation and heat setting processes.

The heat setting takes place at a temperature between the cold crystallization temperature (T_{cc}) and the melt temperature (T_m) of the copolymer composition.

In some cases a surface treatment such as corona, plasma or flame treatment should be employed before winding the film on a roll.

Prior to coating the biaxially oriented PENBB film surface with the antistatic coating composition, the film may be surface treated in a conventional manner by exposure to, e.g. an electric corona discharge, plasma or flame treatment. Electric corona discharge is a conventional surface treatment which is commonly performed on films to enhance their surface qualities, especially their adhesive and printing properties. Electronic corona discharge methods and apparatus are described in U.S. Patent Nos. 3,057,792 and 4,239,973. If the corona treatment followed by the coating occurs before stretch orientation, heating the film before stretch orientation will drive off the water. For biaxially oriented PENBB film, the corona treatment followed by the antistatic coating may occur during the in-line manufacturing process, either before stretch orientation, or between the machine draw and transverse draw of biaxial stretch orientation, or after biaxial stretch orientation. If the corona treatment and coating steps occur after stretch orientation, it is necessary to completely dry the PENBB film before winding. If the corona treatment and coating occur before orientation, or between draw during orientation, the later orientation steps which require the film to be heated would drive off the excess water from the antistatic coating. Preferably, for biaxially oriented PENBB film the corona treatment and subsequent antistatic coating occur between draws during the stretch orientation step.

The PENBB film is coated on the electric corona discharge treated surface preferably with an aqueous dispersion of the antistatic coating composition described below. The coating composition may conveniently be applied as an aqueous dispersion or emulsion using any of the well known coating techniques. For example, the film may be coated by roller coating, spray coating, gravure coating, or slot coating. The heat applied to the film during the subsequent preheating, stretching, and heat setting stages is generally sufficient to evaporate the water and cross-link the antistatic

coating, if a cross-linkable monomer comprises a portion of the antistatic coating.

The coated, biaxially oriented PENBB film may then be heat treated for a period of time necessary to crystallize the film. Crystallization imparts the improved dimensional stability and excellent tensile properties to the PENBB film. The so coated crystallized, biaxially oriented PENBB film is then wound onto a roll.

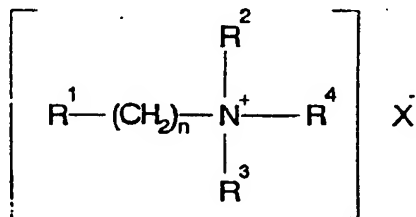
The above description deals with an aqueous antistatic coating composition applied in an in-line (during manufacture) coating process. While this is the preferred process for the biaxially oriented PENBB film, organic solvent-based antistatic coatings as well as off-line coating (after manufacture of the film is complete) is a further aspect of the invention.

The antistatic coating can be composed of:

- I. a composition containing a quarternary ammonium salt (QAS), or
- II. a composition containing an acrylate, styrene derivative or acrylonitrile and an ethylenically unsaturated sulfonate salt, or
- III. a composition containing an organically substituted phosphate.

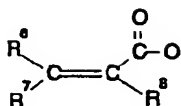
The abovementioned coating compositions are preferably dissolved or dispersed in a liquid medium, such as water, alcohols, ethers, ketones and the like. The following data on weight ratios refer to the solids content of the solutions or dispersions only. The solids content of the solutions or dispersion depends on the film use intended and the physical parameters of the solutions/dispersions and may vary from about 1 to 99 wt.-%, preferably 5 to 70 wt.-%.

Preferably, in the composition containing the QAS (I), the QAS is of the formula



wherein

R^1 is stearamido, $-N^+(R^5)_3X^-$

R^5 being C_1-C_3 alkyl,  with R^6, R^7, R^8 being identical or

different and denoting H or C_1-C_8 alkyl

5 R^2, R^3, R^4 are identical or different and denote H, C_1-C_{20} alkyl, or ω -hydroxy C_1-C_4 alkyl,

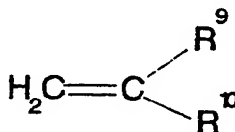
X^- is an anion selected from the group consisting of halogens, sulfates, sulfonates, alkyl sulfonates, carbonates, alkyl carbonates, nitrates, phosphates, alkyl phosphates, and mixtures thereof and

10 n is an integer ranging from 1 to 8.

Preferred QAS are those wherein R^1 is $N(CH_3)_3^+$ or an acrylate or methacrylate radical, R^2 and R^3 are C_1-C_4 alkyl, especially preferred $-CH_3$, R^4 is $-CH_3$, $-CH_2CH_2OH$, $C_{14}-C_{18}$ alkyl, especially tallow, X^- is Cl^- , C_1-C_3 alkyl sulfate, especially methyl sulfate or tosylate, and n is 3.

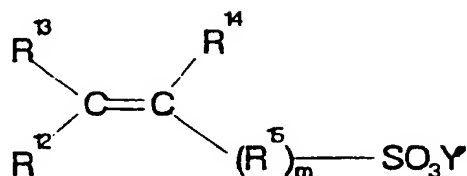
15 Moreover, it is preferred that the QAS is present in the composition in an amount of from about 10 to 80 wt.-% (based on the total weight of the active ingredients of the coating composition). The remainder of the active part of the composition (20 to 90 wt.-%) is a polymeric binder. It may further be desirable to include a suitable self-cross-linking moiety in an amount of up to about 10 wt.-% in the binder.

20 Preferably, in the composition containing the acrylate, styrene derivative or acrylonitrile (II) these are of the formula



25 wherein R^9 is $-H$ or $-CH_3$ and R^{10} is $-COOR^{11}$ (with R^{11} being an alkyl group of 1 to 20 carbon atoms), phenyl or $-CN$.

The ethylenically unsaturated sulfonate salt is preferably one according to the formula:



wherein

5 R^{12} , R^{13} and R^{14} are -H or C_1 - C_4 alkyl,

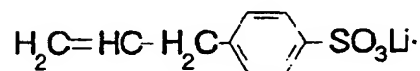
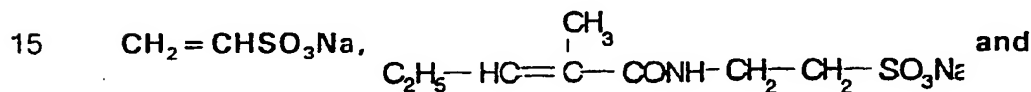
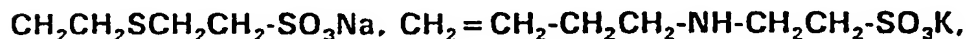
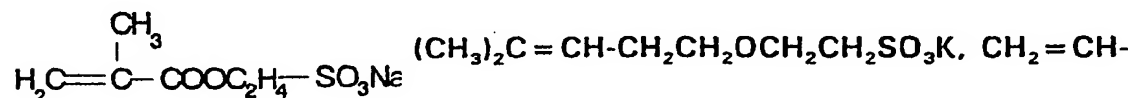
R^{15} is di- C_1 - C_3 -alkylene amine ether or thioether, p-phenylene, C_1 - C_3 alkyl amido, C_1 - C_3 -carboxy or C_1 - C_6 alkylene,

Y is an alkali metal or $-NH(R^{16})_2$

with R^{16} being H or C_1 - C_3 alkyl and

10 m being 0 or 1.

Specific examples of such compounds include sodium allylsulfonate, sodium methallylsulfonate, sodium crotylsulfonate, $CH_3CH=CH(CH_2)_2SO_3NH_4$,



The composition contains the acrylate, styrene derivative or acrylonitrile in about equal amounts based on weight as the ethylenically unsaturated sulfonate salt.

The acrylate based part of the composition II contains a suitable self-cross-linking moiety in an amount of from about 1 to 10 wt.-% based on the acrylate part of the composition.

Moreover, the acrylate based part of composition II may contain up to 5 wt.-% of an ethylenic compound having a carboxy group, which compound is different from the acrylate described above. Suitable ethylenic carboxy-containing compounds are α - β -mono- or di-unsaturated carboxylic acids having 3 to 5 carbon atoms, either in the form of the free acids or their anhydrides or C_1 - C_3 alkyl esters.

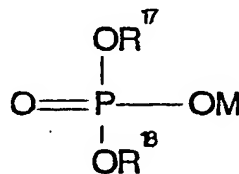
Additionally, the acrylic part of the composition II may include 0 to 29 wt.-% (based on the acrylate part of the composition) of compounds that are copolymerizable with the other components of the acrylic based part; such copolymerizable compounds may include, for example, amides of ethylenic carboxylic acids, such as acrylamide, methacrylamide, diacetone acrylamide and the like; esters between an ethylenic carboxylic acid and an epoxy group-containing alcohol, such as glycidyl acrylate, glycidyl methacrylate and the like; hydroxyalkyl esters of ethylenic carboxylic acids, such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate and the like; esters between ethylenic carboxylic acid and amino group-containing alcohol, such as dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and the like; and compounds having at least two unsaturated groups, such as divinylbenzene, diallyl phthalate, triallyl cyanurate, diethylene glycol dimethacrylate and the like.

The ethylenically unsaturated sulfonate salt part of composition II may include 0 to 70 wt.-% (based on the ethylenically unsaturated sulfonate salt part of the composition) of a different compound copolymerizable with the ethylenically unsaturated sulfonate salt. Such compounds may include α , β -mono- or diunsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, citraconic acid, itaconic acid, maleic acid, fumaric acid and the like; anhydrides of α , β -diunsaturated carboxylic acids, such as maleic anhydride and the like; monoalkyl esters of α , β -diunsaturated carboxylic acids, such as monobutyl maleate, monobutyl fumarate,

monoethyl itaconate and the like; ammonium salts or alkali metal salts of ethylenic carboxylic acids or monoalkyl esters of α,β -diunsaturated carboxylic acids, such as sodium acrylate, ammonium methacrylate and the like; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, isononyl acrylate and the like; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and the like, aromatic vinyl compounds such as styrene, α -methylstyrene, vinyltoluene, ethylvinylbenzene and the like; vinyl cyanides such as acrylonitrile, methacrylonitrile and the like; amides of ethylenic carboxylic acids, such as acrylamide, methacrylamide, diacetone acrylamide and the like; esters between ethylenic carboxylic acids and epoxy group-containing alcohols, such as glycidyl acrylate, glycidyl methacrylate and the like; hydroxyalkyl esters of ethylenic carboxylic acids, such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate and the like; esters between ethylenic carboxylic acids and amino group-containing alcohols, such as dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and the like; and compounds having at least two unsaturated groups, such as divinylbenzene, diallyl phthalate, triallylphthalate, diethylene glycol dimethacrylate and the like.

Preferably, the copolymerization product of the ethylenically unsaturated sulfonate salt and its above-mentioned reaction partner has a molecular weight of about 3000 or more.

Preferably, in the composition containing the organically substituted phosphate (III), these phosphates are of the formula:



wherein

R^{17} is $\text{C}_1\text{-C}_{10}$ alkyl

R^{18} is C_1 - C_{10} alkyl, alkali metal, ammonium, amine cation or hydrogen, and

M is alkali metal, ammonium, an amine cation or hydrogen.

The organically substituted phosphates according to the above formula are present in the coating composition III in an amount of from about 12 to 100 %, preferably 50 to 75 % by weight based on the weight of the coating composition. The remaining portion of the composition is a suitable polymeric binder.

Suitable polymeric binders which may be used include acrylic or methacrylic polymers such as polymethylmethacrylate, copolymers of methyl methacrylate with acrylates such as ethyl acrylate or butyl acrylate, and terpolymers of methyl methacrylate, ethylacrylate and either acrylamide or methacrylamide, or either N-methylolacrylamide or N-methylolmethacrylamide. In many cases it is desirable that the polymeric binder be cross-linkable. This may be accomplished by employing up to about 10 mole-% of a "self cross-linking" functional comonomer into the binder, such as N-methylolacrylamide, or by incorporating a suitable amount of cross linking agent such as melamine formaldehyde or urea formaldehyde condensate capable of reacting with a functional group present in the polymer chain, such as amido, carboxyl, epoxy or hydroxy groups. Other suitable binders include vinyl acetate polymers such as polyvinylacetate and copolymers based on vinylacetate, copolymers containing polymerized vinylidene chloride, i.e., copolymers of vinylidene chloride, acrylic ester and itaconic acid as disclosed in U.S. Pat. No. 2,698,240; and vinylaromatic polymers such as polystyrene, copolymers containing polymerized styrene and polyurethane resin produced from cycloaliphatic, araliphatic, aromatic or preferably an aliphatic polyisocyanate. Examples of suitable polyfunctional isocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, p-xylylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, polymethylene polyphenyl

polyisocyanates and 1,5-naphthylene diisocyanate. 1,6-hexamethylene diisocyanate is particularly preferred. Mixtures of polyfunctional isocyanates may be used as well as polyfunctional isocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

The polymeric polyol component of the polyurethane resin may be a member of any of the chemical classes of polymeric polyols used or proposed to be used in polyurethane formulations. For example, the polymeric polyol may be a polycarbonate, polyesteramide, polyether, polythioether, polyacetal or polyolefin, but preferably a polyester.

The polyester suitably comprises a copolyester, preferably derived from one or more, preferably aromatic, polycarboxylic acids and one or more polyhydric alcohols.

Suitable aromatic polycarboxylic acids for incorporation into the polyester portion of the polyurethane resin include phthalic acid, isophthalic acid, terephthalic acid, 4,4'-bibenzoic acid and 2,6-naphthalic acid or the acid anhydrides or lower-alkyl (up to 10 carbon atoms) esters thereof. Mixtures of two or more thereof, particularly those containing a predominant amount (> 50 mole %) of terephthalic acid, isophthalic acid, 4,4'-bibenzoic acid and/or 2,6-naphthalic acid may also be employed. The aromatic dicarboxylic acid components may be present in an amount greater than 50 mole %, and preferably greater than 80 mole %, of the total acidic components of the polyester.

The polyester may comprise at least one aliphatic or cycloaliphatic dicarboxylic acid, such as cyclohexane-1,4-dicarboxylic acid, adipic acid, sebacic acid, trimellitic acid and/or itaconic acid, and/or polyester-forming equivalents thereof. Adipic acid is particularly preferred. The aliphatic or cycloaliphatic dicarboxylic acid components may be present in an amount of up to about 30 mole % preferably from 0 to 10 mole % of the total acidic components of the polyester.

The polyester may additionally comprise a sulphonated polycarboxylic acid, for example, the ammonium and alkali metal, particularly sodium, salts of 4-sulphophthalic acid, 5-sulpho-isophthalic acid and sulphoterephthalic acid, or the acid anhydrides or lower alkyl (up to 10 carbon atoms) esters thereof. Such acids, or derivatives, are available as alkali metal salts, particularly the sodium sulphonate salt, and are conveniently incorporated in salt form into the polyester portion of the polyurethane resin. The sulphonic acid component is preferably present in a concentration of from 0 to 20 mole %, particularly from 1 to 10 mole %, of the total acidic components of the polyester.

Suitable polyhydric alcohols for incorporation into the polyester include aliphatic, cycloaliphatic and aromatic alkylene glycols, such as ethylene glycol, 1,2-propylene glycol, neopentyl glycol, cyclohexane-1,4-dimethanol and 1,3-propane diol, and particularly aliphatic alkylene-oxy-glycols, such as diethylene glycol. Mixtures of two or more thereof, particularly those containing a predominant amount (> 50 mole %) of ethylene glycol and/or diethylene glycol may also be employed. The polyhydric alcohol is present in a stoichiometrically equivalent amount of approximately 100 mole %.

If desired, the polyester may be modified by the inclusion therein of one or more monohydric alcohols, such as ethylene glycol monobutyl ether, benzyl alcohol and cyclohexanol.

A preferred polyester for incorporation into the polyurethane resin comprises residues of terephthalic acid, isophthalic acid, ethylene glycol, diethylene glycol and optionally a sulphonated polycarboxylic acid. Adipic acid may also be included in the polyester component.

Preferably, the polymeric polyol is of low molecular weight, particularly from about 450 to 9000, and particularly from about 900 to 4500.

If desired, the polyurethane resin may be made with one or more compounds containing a plurality of isocyanate-reactive groups. A suitable additional isocyanate-reactive compound comprises an organic polyol, particularly a short chain aliphatic polyol, preferably neopentyl glycol. An or-

ganic diamine, particularly an aliphatic diamine, may also be included either independently or together with the organic polyol.

If desired, a catalyst for urethane formation, such as dibutyltin dilaurate and/or stannous octoate may be used to assist formation of the polyurethane resin, and a non-reactive solvent may be added before or after formation of the medium to control viscosity. Suitable non-reactive solvents which may be used include acetone, methylethylketone, dimethylformamide, ethylene carbonate, propylene carbonate, diglyme, N-methylpyrrolidone, ethyl acetate, ethylene and propylene glycol diacetates, alkyl ethers of ethylene and propylene glycol monoacetates, toluene, xylene and sterically hindered alcohols such as t-butanol and diacetone alcohol. The preferred solvents are water-miscible solvents such as N-methylpyrrolidone, dimethyl sulphoxide and dialkyl ethers of glycol acetates or mixtures of N-methylpyrrolidone and methyl ethyl ketone. Other suitable solvents include vinyl monomers which are subsequently polymerised.

The polyurethane resins are water dispersible, and a medium comprising an aqueous polyurethane dispersion may be prepared by dispersing the water dispersible, polyurethane resin in an aqueous medium, preferably in the presence of an effective amount of a polyfunctional active hydrogen-containing chain extender.

The resin may be dispersed in water using techniques well known in the art. Preferably, the resin is added to the water with agitation or, alternatively, water may be stirred into the resin.

The polyfunctional active hydrogen-containing chain extender, if employed, is preferably water-soluble, and water itself may be effective. Other suitable extenders include a polyol, an amino alcohol, ammonia, a primary or secondary aliphatic, alicyclic, aromatic, araliphatic or heterocyclic amine especially a diamine, hydrazine or a substituted hydrazine.

Examples of suitable chain extenders useful herein include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, butylene diamine, hexamethylene diamine, cyclohexylene diamine, piperazine, 2-methyl piperazine, phenylene diamine, tolylene diamine, xylylene

diamine, tris (2-aminoethyl) amine, 3,3'-dinitrobenzidine, 4,4'-methylene-bis(2-chloroaniline), 3,3'-dichloro-4,4'-biphenyl diamine, 2,6'-diaminopyridine, 4,4'-diaminodiphenylmethane, menthane diamine, m-xylene diamine, isophorone diamine, and adducts of diethylene triamine with acrylate or its hydrolyzed products. Also, materials such as hydrazine, azines such as acetone azine, substituted hydrazines such as, for example, dimethyl hydrazine, 1,6-hexamethylene-bis-hydrazine, carbodihydrazine, hydrazides of dicarboxylic acids and sulfonic acids such as adipic acid mono- or dihydrazide, oxalic acid dihydrazide, isophthalic acid dihydrazide, tartaric acid dihydrazide, 1,3-phenylene disulfonic acid dihydrazide, ω -amino-caproic acid dihydrazide, hydrazides made by reacting lactones with hydrazines such as γ -hydroxylbutyric hydrazide, bis-semi-carbazide and bis-hydrazide carbonic esters of glycols such as any of the glycols mentioned above.

Where the chain extender is a substance other than water, for example a diamine or hydrazide, it may be added to the aqueous dispersion of the polyurethane resin or, alternatively, it may already be present in the aqueous medium when the resin is dispersed therein.

Desirably, the polyfunctional chain extender should be capable of intra-molecular cross-linking, to improve durability and resistance to solvents. Suitable resinous intra-molecular cross-linking agents comprise epoxy resins, alkyd resins and/or condensation products of an amine, e.g. melamine, diazine, urea, cyclic ethylene urea, cyclic propylene urea, thiourea, cyclic ethylene thiourea, alkyl melamines, aryl melamines, benzoguanamines, guanamines, alkyl guanamines and aryl guanamines with an aldehyde, e.g. formaldehyde. A useful condensation product is that of melamine with formaldehyde. The condensation product may optionally be partially or totally alkoxyated, the alkoxy group preferably being of low molecular weight, such as methoxy, ethoxy, n-butoxy or iso-butoxy. A hexamethoxymethyl melamine condensate is particularly suitable. Another particularly suitable cross-linking agent is a polyaziridine.

Such polyfunctional chain extenders preferably exhibit at least tri

functionality (i.e. three functional groups) to promote inter-molecular cross-linking with the functional groups present in the polyurethane resin.

The chain extension may be conducted at elevated, reduced or ambient temperature. Convenient temperatures are from about 5° to 95°C or more, preferably from about 10° to about 45°C.

The amount of chain extender employed should be approximately equivalent to the free NCO groups in the resin, the ratio of active hydrogens in the chain extender to NCO groups in the resin preferably being in the range from 1-2 : 1.

If desired, and preferably, the antistatic layer may be cross-linked to improve its durability, hardness, cohesive strength and adhesion to the substrate, and to provide resistance to attack by solvents. Cross-linking may be promoted by incorporation into the antistatic composition of any cross-linking agent known to be effective with the binder system in use. Suitable cross-linking agents, especially for polyurethanes, include the condensation product of an amine with an aldehyde. For example, melamine, diazine, urea, cyclic propylene urea, thiourea, cyclic ethylene thiourea, an alkyl melamine, such as butyl melamine, an aryl melamine, a guanamine, an alkyl guanamine, an aryl guanamine, a benzoguanamine, or glycoluril, may be condensed with an aldehyde, such a formaldehyde. The condensation product is preferably alkoxylated, e.g. ethoxylated. A preferred cross-linking agent is a methylated melamine-formaldehyde resin.

The amount of cross-linking agent necessary to promote the required degree of cross-linking may be readily determined by simple experimentation. In general, the cross-linking agent suitable comprises up to 10% and preferably from 2 to 8%, by weight of the total components of the antistatic adherent composition.

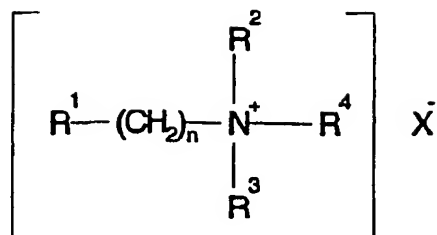
Acceleration of the cross-linking may be effected, if desired, by adding a suitable catalyst to the antistatic composition. A preferred catalyst for use with an amine-formaldehyde cross-linking agent comprises ammonium chloride, ammonium nitrate, phosphoric acid, citric acid, p-toluene sulphonic acid or p-dodecylbenzenesulphonic acid.

The antistatic coating compositions (I), (II) or (III) may be applied to one or both sides of the biaxially oriented PENBB film material at any suitable stage during the manufacture, i.e., after extrusion of the sheet material or before, during, or after biaxially orientation of the sheet. The resultant biaxially oriented PENBB film is found to possess markedly enhanced antistatic properties, good clarity good slip properties and may have good adhesive properties and durability. In addition it exhibits improved mechanical, thermal, hydrolytic and UV stability in comparison to similarly coated biaxially oriented PET film.

WHAT IS CLAIMED IS:

1. Antistatic, mono- or multilayer biaxially oriented copolyester film,
wherein the copolyester is PENBB and wherein at least one surface of the
5 film has been coated with an antistatic coating composition containing
 - I) a quarternary ammonium salt (QAS) and/or
 - II) a two component system consisting of:
 - a) an acrylate, styrene-derivative or acrylonitrile, and
 - b) an ethylenically unsaturated sulfonate salt and/or
 - 10 III) an organically substituted phosphate.
2. Antistatic biaxially oriented film according to claim 1, wherein the
antistatic coating composition contains either
 - I) a QAS, or
 - 15 II) a two component system consisting of:
 - a) an acrylate, styrene-derivative or acrylonitrile, and
 - b) an ethylenically unsaturated sulfonate salt or
 - III) organically substituted phosphate.
- 20 3. Antistatic biaxially oriented film according to claim 1 or 2, wherein
the copolyester film is a monolayer film.
4. Antistatic biaxially oriented film according to any one or more of the
preceding claims, wherein one surface of the film has been coated with the
25 antistatic coating composition.
5. Antistatic biaxially oriented film according to any one or more of the
preceding claims, wherein the QAS is of the formula

20



wherein

R^1 is stearamido or $N^+(R^5)_3X^-$

R^5 being C_1 - C_3 alkyl or with

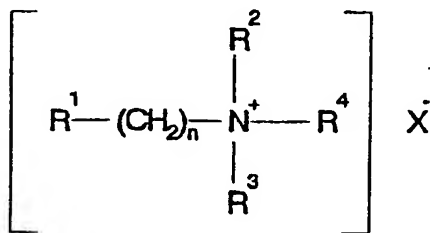
5 R^6 , R^7 and R^8 being identical or different, denoting H or C_1 - C_8 alkyl

R^2 , R^3 and R^4 are identical or different and denote H, C_1 - C_{20} alkyl or ω -hydroxy C_1 - C_4 alkyl

X^- is an anion selected from the group consisting of F^- , Cl^- , Br^- , sulfates, sulfonates, alkyl sulfonates, carbonates, alkyl carbonates, nitrates, phosphates, alkyl phosphates and mixtures thereof and

10 n is an integer ranging from 1 to 8.

6. Antistatic biaxially oriented film according to any one or more of the preceding claims, wherein the QAS is of the formula



wherein

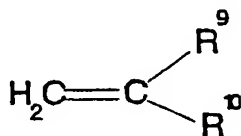
R^1 is $N(CH_3)_3^+$ or an acrylate or methacrylate radical,

R^2 and R^3 are C_1 - C_4 alkyl,

20 R^4 is CH_3 , CH_2CH_2OH or C_{14} - C_{18} -alkyl,

X⁻ is Cl⁻, C₁-C₃ alkyl sulfate or tosylate and
n is 3.

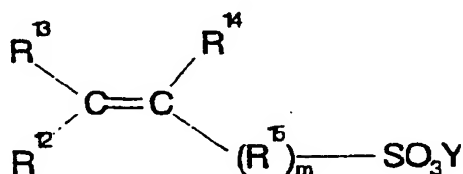
7. Antistatic biaxially oriented film according to any one or more of the
preceding claims, wherein the acrylate, styrene-derivative or acrylonitrile
are of the formula



wherein

- R⁹ is H or CH₃ and
R¹⁰ is COOR¹¹, with R¹¹ being a C₁-C₂₀ alkyl group or
R¹⁰ is phenyl or -CN.

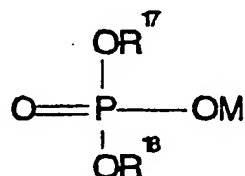
8. Antistatic biaxially oriented film according to any one or more of the
preceding claims, wherein the ethylenically unsaturated sulfonate salt is
one of the formula



wherein

- R¹², R¹³ and R¹⁴ are H or C₁-C₄ alkyl,
R¹⁵ is di-C₁-C₃-alkylene amine, di-C₁-C₃-alkylene ether, di-C₁-C₃-alkylene
thioether, p-phenylene, C₁-C₃-alkylamido, C₁-C₃-carboxy or C₁-C₆-alkylene
Y is an alkali metal or N(R¹⁶)₃ with R¹⁶ being H or C₁-C₃-alkyl and
m being 0 or 1.

9. Antistatic biaxially oriented film according to any one or more of the preceding claims, wherein the organically substituted phosphates are of the formula



5 wherein

R^{17} is $\text{C}_1\text{-C}_{10}$ -alkyl,

R^{18} is $\text{C}_1\text{-C}_{10}$ -alkyl, an alkali metal, ammonium, an amine cation or hydrogen and

M is an alkali metal, ammonium, amine cation or hydrogen.

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10. Antistatic biaxially oriented film according to any one or more of the preceding claims, wherein the birefringence of the film is < 0.2 and the IV-value of the PENBB is > 0.5 dl/g.

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11. Use of a film according to claim 1 as packaging material.

12. Use of a film according to claim 1 as reprographic film.

13. Use of a film according to claim 1 as microfilm.

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14. Use of a film according to claim 1 as magnetic tape substrate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10701

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 27/06

US CL :428/910, 483, 520, 522

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/910, 483, 520, 522

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,642,263 (CULBERTSON) 10 FEBRUARY 1987. See Example 1, column 6.	1-3

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	*T* Inter document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

23 FEBRUARY 1993

Date of mailing of the international search report

06 APR 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

1. International application No.
PCT/US92/10701

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 11-14
because they relate to subject matter not required to be searched by this Authority, namely:

Claims 11-14 are directed to a "Use". PCT Article 17(2)(a)(i). "Use" claims not in method terminology is not searched by this authority.
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.